

We claim:

1. A process which catalytically dehydrogenates paraffin hydrocarbon feedstocks over a bed of metallic catalyst in a membrane based dehydrogenation reactor to produce olefins and hydrogen, with the permeate stream from the membrane reactor to consist mainly of hydrogen, olefin, and lesser amounts of permeated paraffin, with the non-permeate stream from the membrane reactor to consist of olefin, hydrogen and unreacted paraffin, with the membrane in the dehydrogenation reactor to be an inorganic membrane, inorganic-metal membrane, or metal based membrane made by one or more of the following ceramic oxides:

alumina (Al_2O_3), ✓

titania (TiO_2), ✓

silica (SiO_2), ✓

zirconia (ZrO_2), ✓

mixed with one or more of the following catalytic metals: Pt (platinum), Cr (chromium), Pd (palladium), Cu (copper), Zn (zinc), V (vanadium), Mg (magnesium), Ru (ruthenium), Rh (rhodium), Ni (nickel), Fe (iron), Sn (tin), Mo (molybdenum),

or with the membrane to be made by the following metal and metal alloys:

Palladium,

Palladium-Silver,

Palladium-Platinum,

Palladium-Platinum-Silver,

Vanadium,

Palladium-Vanadium,

Palladium-Vanadium-Silver,

Niobium,

Palladium-Niobium,

Palladium-Niobium-Silver,

Tantalum,

Palladium-Tantalum,

Palladium-Tantalum-Silver

Zirconium,

Palladium-Zirconium,

Palladium-Zirconium-Silver,

with the permeate and reject streams to merge in the downstream of the membrane reactor by re-compressing the permeate stream into the same pressure with the reject stream, with the combined one stream to pass through a heat exchanger to reduce its temperature by exchanging heat and generating steam, with the cooled mixture stream to be fed into a polymerization reactor for polymerization reaction to a polyolefin, after mixing with a bypass-fed solvent in vapor, gas, or liquid phase, with the last polymerization reactor to be of gas-phase, fluid bed type or of slurry-solution phase, stirred bed type, with the formed polymer to exit from the last reactor in the form of particles, granules or foam, with the hydrogen produced from the dehydrogenation reaction to be used in the polymerization reactor as a chain transfer agent to regulate and reduce the polymer molecular weight, with the unreacted paraffin from the

dehydrogenation reactor to be used in the polymerization reactor as a diluent, solvent or heat removing medium, with the unreacted olefin and paraffin from the polymerization to exit from the top of the last reactor and enter into a membrane based separator which separates olefin from paraffin and recycles the olefin into the inlet of the polymerization reactor and the paraffin into the inlet of the initial membrane dehydrogenation reactor, with the membrane in the downstream separator to be a dense, porous, or liquid like synthetic polymer or composite type membrane containing one or more of the following metal ions, Cu (copper), Ag (silver), Cr (chromium), Fe (iron), Zn (zinc), Sn (tin), Co (cobalt), Ni (nickel), Mn (manganese), V (vanadium), Ti (titanium), Ru (ruthenium), Rh (rhodium), and with the polymer material of the membrane to consist by one or more of the following: poly(methyl methacrylate), poly (methyl acrylate), polystyrene, poly(vinyl acetate), poly(vinyl pyrrolidone), poly(vinyl carbazole), poly(vinyl stearate), poly(β -propiolactone), polydiketene, polytrioxane, poly(acrylic ester), polyacrylonitrile, polymethacrylonitrile, poly(acrylic acid), poly(methacrylic acid), poly(vinyl chloride), poly(vinylidene chloride), polytetrafluoroethylene, polychlorotrifluoroethylene, poly(vinyl fluoride), poly(vinylidene fluoride), polyimides, polycarbonates, polysulfones, polybenzimidazoles, polyphosphazenes, polyamides, polycaprolactams, parylenes, polysiloxanes.

2. The process of claim 1 wherein the initial feedstock is either ethane or propane and the dehydrogenation reaction of ethane to ethylene or of propane to propylene is occurring respectively in the catalytic membrane dehydrogenation reactor, and the conversion of ethylene to polyethylene or of propylene to polypropylene is occurring in the next polymerization reactor with polyethylene or polypropylene respectively to be the final polymer product.

3. The process of claim 1 wherein the initial feedstock is either n-butane or i-butane or 4-methylpentane, and the dehydrogenation reaction of n-butane to butene-1, or of i-butane to isobutene, or 4-methylpentane to 4-methylpentene-1, is occurring in the membrane catalytic dehydrogenation reactor and the conversion of butene-1 to poly(butene-1), or of isobutene to poly(isobutene), or of 4-methylpentene-1 to poly(4-methylpentene-1), is occurring in the next polymerization reactor with poly(butene-1) or poly(isobutene) or poly(4-methylpentene-1) to be the final polymer product.

4. The process of claim 1 wherein the initial feedstock is ethylbenzene and the dehydrogenation reaction of ethylbenzene to styrene is occurring in the membrane catalytic dehydrogenation reactor and the conversion of styrene to poly(styrene) is occurring in the next polymerization reactor with poly(styrene) to be the final polymer product.

5. The process of claim 1 wherein the initial feedstock is either butene-1 or butene-2 or a mixture of both alkenes, and the dehydrogenation reaction of butene-1 to 1,3-butadiene or of butene-2 to 1,3-butadiene or both these reactions are occurring in the membrane catalytic dehydrogenation reactor and the conversion of 1,3-butadiene to poly(1,3-butadiene) is occurring in the next polymerization reactor with poly(1,3-butadiene) to be the final polymer product.

6. The process of claim 1 wherein the feedstock in the initial dehydrogenation reactor is one of the following:

propane for final production of propylene-ethylene copolymers,
ethane, propane mixture for final production of ethylene-propylene copolymers,
n-butane or i-butane for final production of butylene-propylene-ethylene copolymers, or butylene-propylene copolymers, or butylene-ethylene copolymers,
another paraffin, or another saturated or unsaturated hydrocarbon, or naphtha, for dehydrogenation and final polymerization of the dehydrogenated compounds into the corresponding polymers.

7. The process of claim 1 wherein the initial membrane dehydrogenation reactor is replaced by a non-permeable fixed bed catalytic reactor or by a non-permeable, non-catalytic thermal cracker, with all products and unreacted reactants to exit from the single outlet and directed after cooling into the polymerization reactor for production of polyolefins.

8. The process of claim 7 wherein the feedstock in the initial dehydrogenation reactor is one of the following:

ethane, for final production of polyethylene,
propane, for final production of polypropylene,
ethane, propane mixture for final production of ethylene-propylene copolymers,
n-butane, for final production of poly(butene-1),
i-butane, for final production of poly(isobutene),
n-butane or i-butane for final production of butylene-propylene-ethylene copolymers, or butylene-propylene copolymers, or butylene-ethylene copolymers,
4-methylpentane-1 for final production of poly(4-methylpentene-1),
ethylbenzene for final production of poly(styrene),
butene-1 for final production of 1,3-butadiene,
butene-2 for final production of 1,3-butadiene,
butene-1 and butene-2 mixture, for final production of 1,3-butadiene,
another paraffin, or another saturated or unsaturated hydrocarbon, or naphtha, for dehydrogenation and final polymerization of the dehydrogenated compounds into the corresponding polymers.

9. The process of claim 1 wherein the metal or metal alloy membrane allows only hydrogen to permeate through into the permeate stream, and the reject stream contains no hydrogen or only small amounts of non-permeated hydrogen mixed with the olefin product and the unreacted paraffin, and with the final polyolefin product from the polymerization reactor to be of high molecular weight due to the absence of the hydrogen chain transfer effect.

10. The process of claim 9 wherein the feedstock in the initial metal membrane dehydrogenation reactor is one of the following components:

ethane, for final production of polyethylene,
propane, for final production of polypropylene,
ethane, propane mixture for final production of ethylene-propylene copolymers,
n-butane, for final production of poly(butene-1),
i-butane, for final production of poly(isobutene),
n-butane or i-butane for final production of butylene-propylene-ethylene copolymers, or butylene-propylene copolymers, or butylene-ethylene copolymers,
4-methylpentane-1 for final production of poly(4-methylpentene-1),
ethylbenzene for final production of poly(styrene),
butene-1 for final production of 1,3-butadiene,
butene-2 for final production of 1,3-butadiene,
butene-1 and butene-2 mixture, for final production of 1,3-butadiene,
another paraffin, or another saturated or unsaturated hydrocarbon, or naphtha, for dehydrogenation and final polymerization of the dehydrogenated compounds into the corresponding polymers.

11. A process which integrates a membrane separator and a polymerization reactor into a single module, with the feed in separator to consist of an olefin-paraffin mixture, with the olefin to be separated from the paraffin by the use of a membrane in the membrane permeator, with the membrane to be a dense, porous or liquid like synthetic polymer or composite membrane containing one or more of the following metal ions: Cu (copper), Ag (silver), Cr (chromium), Fe (iron), Zn (zinc), Tin (Sn), Co (cobalt), Ni (nickel), Mn (manganese), V (vanadium), Ti (titanium), Ru (ruthenium), Rh (rhodium), with the gas flow in the membrane separator to be of plug flow, mixed (stirred) flow or fluid bed flow type, with the non-permeate paraffin to exit as reject stream from the permeator exit, with the permeate through the membrane olefin to undergo fluidization without or with stirring with gas phase polymerization and conversion into polyolefin at the same time in the adjacent integrated reactor module by using suitable metallic catalyst in the form of fluidized powder or particles, with the unreacted olefin from the polymerization to exit from the top of the integrated polymerization reactor and after passing through a cooler to remove the exothermic heat of polymerization, to be recycled back into the inlet of polymerization reactor for continuous polymerization, with the produced polyolefin product to exit from a separate exit in the form of particles, granules, or foam, and finally with the polymer material of the membrane in the integrated separator

to consist by one or more of the following: poly(methyl methacrylate), poly (methyl acrylate), polystyrene, poly(vinyl acetate), poly(vinyl pyrrolidone), poly(vinyl carbazole), poly(vinyl stearate), poly(β -propiolactone), polydiketene, polytrioxane, poly(acrylic ester), polyacrylonitrile, polymethacrylonitrile, poly(acrylic acid), poly(methacrylic acid), poly(vinyl chloride), poly(vinylidene chloride), polytetrafluoroethylene, polychlorotrifluoroethylene, poly(vinyl fluoride), poly(vinylidene fluoride), polyimides, polycarbonates, polysulfones, polybenzimidazoles, polyphosphazenes, polyamides, polycaprolactams, parylenes, polysiloxanes.

12. The process of claim 11 wherein the feedstock in the inlet of the integrated membrane separator-polymerization reactor is one of the following mixtures:

- ethane, ethylene mixture for final production of polyethylene,
- propane, propylene mixture for final production of polypropylene,
- ethane, propane, ethylene, propylene mixture for final production of ethylene-propylene copolymers,
- n-butane, butene-1 mixture for final production of poly(butene-1),
- i-butane, isobutane mixture for final production of poly(isobutene),
- 4-methylpentane-1, 4-methylpentene-1 mixture for final production of poly(4-methylpentene-1),
- mixtures of hydrocarbons with butenes, propylene, ethylene for final production of C₂-C₄ copolymers,
- another paraffin, olefin mixture or hydrocarbon, olefin mixture, or naphtha mixtures, for olefin separation via the membrane and final polymerization of the separated olefin into the corresponding polymer.

13. A process which integrates a membrane catalytic reactor and a polymerization reactor into a single module, with the feed in the membrane reactor to consists of a paraffin which is dehydrogenated into an olefin by the use of metallic catalyst, with the gas flow in the membrane reactor to be of plug-flow, mixed (stirred) flow, or fluid bed flow type, with products olefin and hydrogen to be produced from the dehydrogenation reaction and permeate through the membrane into the adjacent reactor side of the integrated reaction-separation module, with the membrane to be of dense or porous structure of inorganic, inorganic-metal, inorganic-polymer or composite nature containing one or more of the following metal ions: Cu (copper), Ag (silver), Cr (chromium), Fe (iron), Zn (zinc), Sn (tin), Co (cobalt), Ni (nickel), Mn (manganese), V (vanadium), Ti (titanium), Ruthenium (Ru), Rhodium (Rh), with the non-permeate stream containing mainly unreacted paraffin and traces of olefin and hydrogen to exit as reject stream from the membrane reactor outlet and recycled back into the membrane reactor inlet for continuous dehydrogenation, with the permeate from the membrane olefin product to undergo fluidization without or with stirring and gas phase polymerization conversion into polyolefin in the adjacent integrated polymerization reaction module by using suitable metallic catalyst in the form of powder or particles, with the permeate hydrogen to be used in polymerization as a chain transfer agent to regulate and reduce the polymer molecular

weight, with the unreacted olefin to exit from the top of the polymerization reactor and after passing through a cooler to remove the exothermic heat of polymerization, to be recycled back into the reactor for continuous polymerization, with the produced polyolefin product to exit from a separate exit in the form of particles, granules or foam,

with the membrane in the integrated module to be made by one or more of the following ceramic oxides:

alumina (Al_2O_3),

titania (TiO_2),

silica (SiO_2),

zirconia (ZrO_2),

mixed with one or more of the following catalytic metals: Pt (platinum), Cr (chromium), Pd (palladium), Cu (copper), Zn (zinc), V (vanadium), Mg (magnesium), Ru (ruthenium), Rh (rhodium), Ni (nickel), Fe (iron), Sn (tin), Mo (molybdenum),

and possibly with one or more of the following polymer materials: poly(methyl methacrylate), poly(methyl acrylate), polystyrene, poly(vinyl acetate), poly(vinyl pyrrolidone), poly(vinyl carbazole), poly(vinyl stearate), poly(β -propiolactone), polydiketene, polytrioxane, poly(acrylic ester), polyacrylonitrile, polymethacrylonitrile, poly(acrylic acid), poly(methacrylic acid), poly(vinyl chloride), poly(vinylidene chloride), polytetrafluoroethylene, polychlorotrifluoroethylene, poly(vinyl fluoride), poly(vinylidene fluoride), polyimides, polycarbonates, polysulfones, polybenzimidazoles, polyphosphazenes, polyamides, polycaprolactams, parylenes, polysiloxanes.

14. The process of claim 13 wherein the feedstock in the inlet of the integrated membrane reactor-polymerization reactor module is one of the following:

ethane for final production of polyethylene,

propane for final production of polypropylene,

ethane, propane mixture for final production of ethylene-propylene copolymers,

n-butane for final production of poly(butene-1),

i-butane for final production of poly(isobutene),

4-methylpentane-1 for final production of poly(4-methylpentene-1),

ethylbenzene for final production of poly(styrene),

butene-1 for final production of 1,3-butadiene,

butene-2 for final production of 1,3-butadiene,

butene-1, butene-2 for final production of 1,3-butadiene,

mixtures of butanes, propane, ethane or naphtha for final production of $\text{C}_2\text{-C}_4$ copolymers,

another paraffin or hydrocarbon feed for dehydrogenation into an olefin and final polymerization of the separated olefin into the corresponding polymer.

15. The process of claim 9 which relates with the ethane to ethylene dehydrogenation reaction and the production of ethylene, wherein oxygen or air with or without a diluent is added into the consecutive reactor and the consecutive reactor is replaced by a catalytic ethylene oxide-direct production reactor.

16. The process of claim 15 wherein the ethylene oxide product is fed into a next, downstream slurry-liquid phase reactor for production of ethylene glycol by hydration.

17. The process of claim 9 which relates with the ethane to ethylene dehydrogenation reaction and the production of ethylene, wherein oxygen or air with or without a diluent is added into the consecutive reactor and the consecutive reactor is replaced by a slurry-liquid phase catalytic reactor for direct production of acetaldehyde.

18. The process of claim 9 which relates with the propane to propylene dehydrogenation reaction and the production of propylene, wherein oxygen with or without steam, or air with or without steam are added into the consecutive reactor and the consecutive reactor is replaced by a catalytic reactor for the production of acrolein and acrylic acid.

19. The process of claim 9 which relates with the propane to propylene dehydrogenation reaction and the production of propylene, wherein oxygen and ammonia, or air and ammonia are added into the consecutive reactor and the consecutive reactor is replaced by a catalytic reactor for the production of acrylonitrile.

20. The process of claim 9 which relates with the propane to propylene dehydrogenation reaction and the production of propylene, wherein a hydroperoxide, or a mixture of ethylbenzene with air, or isobutane with air, are added into the consecutive reactor and the consecutive reactor is replaced by a catalytic reactor for the production of propylene oxide, with propylene oxide to optionally hydrated in a next downstream reactor for production of propylene glycol.

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